



(1) Publication number:

0 402 181 A1

٠,٠

12

EUROPEAN PATENT APPLICATION

21 Application number: 90306405.3

(5) Int. Cl.⁵: **B05D** 1/38, **B05D** 7/16, **B05D** 5/06

2 Date of filing: 12.06.90

3 Priority: 12.06.89 JP 146673/89

Date of publication of application:12.12.90 Bulletin 90/50

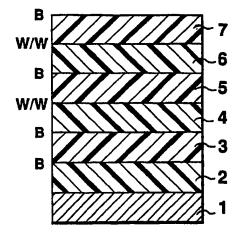
Designated Contracting States:
DE GB

Applicant: NISSAN MOTOR CO., LTD. No.2, Takara-cho, Kanagawa-ku Yokohama City(JP) Inventor: Yamanaka, Masahiko
Tsurumaki-shataku B-206
No. 1176, Tsurumaki
Hadano City Kanagawa Prefecture(JP)
Inventor: Nakasuji, Hideki
No. 3-4710-1, Sobudai
Zama City(JP)

Representative: Godwin, Edgar James et al MARKS & CLERK 57-60 Lincoln's Inn Fields London, WC2A 3LS(GB)

- Method for forming Japan-like paint film.
- The method is applied to a steel plate (1) forming part of an automotive vehicle outer panel. A first coating layer of an electrodeposition paint (2) and an intermediate coat paint (3) is formed on the surface of the plate (1). Subsequently, a second coating layer is formed by applying a base coat paint (4) and a colorless clear paint (5), wet-on-wet, and is baked to be hardened. The base coat paint (4) contains aluminum powder in an amount of not more than 13% by weight relative to the solid content of the base coat paint. Lastly, a third coating layer is formed by applying a colored clear paint (6) and a colorless clear paint (7) on the second coating layer, wet-on-wet, and is baked to be hardened. The colored clear paint (6) contains particulate pigment whose content is 0.5 to 5% by weight relative to the solid content of the colored clear paint and whose particle size is 0.01 to 0.4 μm.

FIG.1



METHOD FOR FORMING JAPAN-LIKE PAINT FILM

This invention relates to a method for forming a japan-like paint film, having transparency and deepness feelings, on the surface of an object such as a steel plate of an automotive vehicle outer panel.

Hitherto a method for forming a japan-like paint film having transparency and deepness feelings has been proposed. In this method, an electrodeposition paint and an intermediate coat paint are coated on the surface of a steel plate and baked to be hardened. Thereafter, a base coat paint containing pigment and aluminum and a colored clear paint containing dye are coated in a wet-on-wet manner on the surface of the baked electrodeposition and intermediate coat paints, and are then baked, thereby to form the desired paint film.

However, difficulties have been encountered in the japan-like paint film formed by such a method, in which the formed paint film deteriorates during a long time outdoor exposure so as to suffer color-change, discoloration, blistering and the like. These are resulted from the fact that dye in the paint film has a low weatherability. Under such a deterioration, the initial transparency and deepness feelings of the paint film cannot be restored even if waxing is made on the paint film, thus degrading the commercial value of an article coated with the paint film.

What is desired is a method for forming a japan-like paint film which can solve the problems encountered in conventional ones.

It would also be desirable to be able to provide an improved method for forming a japan-like paint film which can be high in transparency and deepness feelings and high in weatherability, providing a new image and a high commercial value to an article to be coated with the paint film.

A method forming a japan-like paint film, according to the present invention, comprises the following steps in the sequence set forth: a) coating an electrodeposition paint and an intermediate coat paint which are baked to form a first coating layer; b) coating a base coat paint and a colorless clear paint on the first coating layer in a wet-on-wet manner, the base coat paint containing aluminum powder in an amount of not more than 13% by weight relative to the solid content of the base coat paint; c) baking the coated base coat paint and colorless clear paint to form a second coating layer on the first coating layer; d) coating a colored clear paint and a colorless clear paint on the second coating layer in a wet-on-wet manner, the colored clear paint containing particulate pigment in an amount ranging from 0.5 to 5% by weight relative to the solid content of the colored clear paint, the particulate pigment having a particle size ranging from 0.01 to 0.4 μ m; and e) baking the coated colored clear paint and colorless clear paint to form a third coating layer on the second coating layer.

The invention will be described further by way of example only, with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The single figure, Fig. 1, is an enlarged and fragmentary sectional view of a paint film coated on an article, by a method according to the present invention.

DETAILED DESCRIPTION

15

According to the present invention, a method forming a japan-like paint film comprises the following steps in the sequence set forth: a) coating an electrodeposition paint and an intermediate coat paint which are baked to form a first coating layer; b) coating a base coat paint and a colorless clear paint on the first coating layer in a wet-on-wet manner, the base coat paint containing aluminum powder in an amount of not more than 13% by weight relative to the solid content of the base coat paint; c) baking the coated base coat paint and colorless clear paint to form a second coating layer on the first coating layer; d) coating a colored clear paint and a colorless clear paint on the second coating layer in a wet-on-wet manner, the colored clear paint containing particulate pigment in an amount ranging from 0.5 to 5% by weight relative to the solid content of the colored clear paint, the particulate pigment having a particle size ranging from 0.01 to 0.4 μ m; and e) baking the coated colored clear paint and colorless clear paint to form a third coating layer on the second coating layer. Meant by the term "japan" is a Japanese laquer or "Urushi" in Japanese.

In a preferred procedure according to the present invention, first the electrodeposition paint is coated on a steel plate or sheet which, for example, forms part of an automotive vehicle outer panel. Then the electrodeposition paint is baked to be hardened. An intermediate coat paint is coated on the baked

electrodeposition paint and baked to be hardened. The thus formed two hardened layers constitute the first coating layer.

Subsequently, a base coat paint and a colorless clear paint are successively coated on the hardened intermediate coat paint, in a wet-on-wet manner in which the colorless clear paint is coated on the base coat paint which has still been in a wet state. Then the thus coated base coat paint and colorless clear paint are simultaneously baked to be hardened, thereby forming the second coating layer.

Next, the colored clear paint and the colorless clear paint are successively coated on the second coating layer in a wet-on-wet manner in which the colorless clear paint is coated on the colored clear paint which has still been in a wet state. Then, the thus coated colored clear paint and colorless clear paint are baked to be hardened, thereby forming the third coating layer. Thus, each of the second and third coating layers is formed by a so-called two coatings and one baking manner.

As a result, the Japan-like paint film as shown in Fig. 1 is obtained. In Fig. 1, the reference numeral 1 denotes the steel plate, 2 the electrodeposition paint, 3 the intermediate coat paint, 4 the base coat, 5 the colorless clear paint, 6 the colored clear paint, and 7 colorless clear paint. In Fig. 1, the characters B and W/W respectively designate "baking" and "coating in the wet-on-wet manner".

The base coat paint, the colorless clear paint, and the colored clear paint are preferably formed of acrylic polyol and/or acrylic polyol modified with fluororesin; and a hardener such as melamine or isocyanate is preferably used.

The base coat paint contains pigment and aluminum powder. The content of the aluminum powder is 20 not more than 13% by weight relative to the solid content of the base coat paint. The solid content of the aluminum powder is preferably not more than 8% by weight in caseswhere the base coat paint is in a red color system including red and red-like colors or in cases where the base coat paint is in a blue color system including blue and blue-like colors. It is also preferable that the content of the aluminum powder is not more than 0.5% by weight in caseswhere the base coat paint is in black color.

The colored clear paint is colored by transparent coloring agent such as dye as usual. However, in this case, the colored clear paint contains particulate pigment in an amount 0.5 to 5%, preferably 2 to 4% by weight relative to the solid content of the paint. The particle size of the atomized pigment is within a range from 0.01 to 0. 4 µm. The particle size is preferably within a range from 0.2 to 0.4 µm in caseswhere the colored clear paint is in the red color system or in cases where the colored clear paint is in the blue color system. It will be understood that the colorless clear paint has no coloring agent such as dye.

EXAMPLES

In order to evaluate the japan-like paint film of the present invention, Examples 1 to 5 will be discussed with reference to Comparative Examples 1 to 4 which are not within the scope of the present invention.

Examples 1 to 5 and Comparative Examples 1 to 3

A cold-rolled steel plate having dimensions of 70 mm x 150 mm x 0.8 mm was treated with zinc phosphate ("Grano-dine DP4000", the trade name of Nippon Paint Co., Ltd. in Japan). Then, an undercoat paint ("Powertop U100", the trade name of Nippon Paint Co., Ltd. in Japan) was coated under electrodeposition to form a coating layer having a thickness of 20 µm. This under-coat paint was baked at 175°C for 30 minutes. Subsequently, an intermediate coat paint ("Orga S93", the trade name of Nippon Paint Co., Ltd. in Japan) was coated on the surface of the electrodeposited under coat paint by an air spray to form a coating layer having a thickness of 35 µm. This coating layer of the intermediate coat paint was baked at 140 C for 30 minutes.

Next, a base coat paint shown in Tables 1 and 2 was coated on the coating layer of the intermediate coat paint so as to have a thickness of 15 µm. Then, a colorless clear paint was coated on the base coat paint in a wet-on-wet manner so as to have a thickness of 15 µm. In other words, the colorless clear paint was coated on the base coat paint which had been still wet. The thus coated base coat paint and colorless clear paint were baked at 140°C for 30 minutes thereby to form a coating layer. Furthermore, a colored clear paint was coated on the colorless clear paint so as to have a thickness of 15 µm. Additionally, a colorless clear paint was coated on the colored clear paint in a wet-on-wet manner so as to have a thickness of 15 µm. The thus coated color and colorless paints were baked at 140 °C for 30 minutes to form a coating layer. As a result, each specimen or test plate of Examples 1 to 5 and Comparative Examples 1 to 3 was prepared.

25

35

Comparative Example 4

Formation of the coating layers of the undercoat paint and the intermediate coat paint were made on the steel plate in the same manner as that in the above Examples and Comparative Examples. Then, a base coat paint as shown in Tables 1 and 2 was coated on the coating layer of the intermediate coat paint so as to have a thickness of 15µm. Additionally, the colorless clear paint shown in Table 1 was coated on the base coat paint in a wet-on-wet manner so as to have a thickness of 15 µm. The thus coated base coat paint and colorless clear paint were baked at 140 °C for 30 minutes, thereby to form a coating layer. Furthermore, the colorless clear paint shown in Table 1 was coated on the thus formed coating layer, and baked at 140 °C for 30 minutes. As a result, a specimen or test plate of Example 4 was prepared.

EVALUATION TEST

15

20

40

50

55

Evaluation tests of the below-listed items were conducted on the above specimens or test plates of the Examples and the Comparative Examples to obtain test results shown in Table 3.

(1) Adhesion of Paint film by Cross-cut test

A plurality of straight linear cuts were parallely made on the surface of the paint film with a distance of 2 mm between the adjacent lines. Then, a plurality of straight linear cuts were parallely made on the surface of the paint film in a manner to cross the former straight linear cut thereby to form a plurality of square cut pieces. All the straight linear cuts reached the surface of the steel plate. An adhesive tape was applied on the surface of 25 square cut pieces. Then, the adhesive tape was peeled off from the surface of the paint film at a stretch, and the peeled-off condition of 25 square cut pieces of the paint film was observed to evaluate the adherence of the paint film. If all 25 square cut pieces remained not peeled off as shown as "25/25" in Table 3, the adherence of the paint film was evaluated excellent.

(2) Weatherability

A weatherability test or light radiation was carried out on each of the specimens or sample plates by using a sunshine weather-ometer (produced by Suga Test Instrument Co., Ltd. in Japan) under a test condition in which the temperature of a black (standard) panel was 63 °C; rain was used; and the test time was 750 hrs. After this test, the following items were evaluated:

a) Gloss Retention Rate (GR):

GR (Gloss Retention Rate) % =

Gloss after weatherability test x 100 Gloss before weatherability test

b) Color Difference (ΔΕ):
ΔΕ (Color Difference) was measured by a SM Color Computer produced by Suga Test Instrument Co., Ltd. in Japan. The color difference was a difference in color between the colors of the specimen before and after the weatherability test.

(3) Feelings

- a) Transparency feeling: The transparency feeling of each specimen was evaluated from the surface of the paint film by visual observation.
- b) Deepness feeling: The deepness feeling of each specimen was evaluated from the surface of the paint film by visual observation.

TABLE 1

 $(A)/(B)^{1)}$ Acrylic polyol (A) Melamine (B) Coatax LU651 2) (trade name of 70/30 Cymel 327 (trade name of Base coat Toray Co., Ltd. in Japan) Mitsui Cynamid Co., Ltd. in paint Japan Dianal LR532 3) (trade name of 70/30 Cymel 327 Colorless Mitsuibishi Rayon Co., Ltd. in clear paint Japan) 70/30 Cymel 327 Colored Dianal LR532 clear paint Note

1): Ratio in resin solid content

2): Non-volatile content ... 50% by weight

3): Non-volatile content ... 60% by weight

TABLE 2

25			•		Example	Comparative Example					
			1	2	3	4	5	1	2	3	4
30	Base coat paint	Content of aluminum (wt%)	8 (0)	8 (0)	8 (0)	5	13	20	8 (0)	8 (0)	10 (0.1)
	Color clear	Particle size of pigment (µm)	0.3 (0.03)	0.3 (0.03)	0.3 (0.03)	0.3 (0.03)	0.3 (0.03)	0.3 (0.03)	1.0	0.3 (0.03)	1.0 (0.1)
35	paint	Concentration of pigment (wt%)	0.5	3	5	3	3	0.5	3	10	10
	Note: A	valve within () repres	ents that	in case o	f black co	olor.					

TABLE 3

ſ					Example		Comparative Example					
45			1	2	3	4	5	1	2	3	4	
	Adhesion	25/25	25/25	25/25	25/25	25/25	25/25	25/25	25/25	25/25		
Ì	Weatherability	GR	80	85	90	87	85	70	80	85	75	
50		ΔΕ	1.9	1.8	1.5	1.8	2.1	3.5	2.1	2.2	3.0	
	Transparency feeling		good	good	good	good	good	good	bad	bad	bad	
	Deepness feelin	good	good	good	good	good	bad	bad	bad	bad		

40

5

10

15

20

- 1. A method for forming a japan-like paint film, comprising the following steps in the sequence set forth:
- a) coating an electrodeposition paint (2) and intermediate coat paint (3), which are baked to form a first coating layer;
- b) coating a base coat paint (4), optionally containing pigment, and a colorless clear paint (5) on the first coating layer in a wet-on-wet manner, the base coat paint (4) containing aluminum powder in an amount of not more than 13% by weight relative to the solid content of the base coat paint;
- c) baking the base coat paint (4) and colorless clear paint (5) to form a second coating layer on the first coating layer;
- d) coating a colored clear paint (6) and a colorless clear paint (7) on the second coating layer in a wet-on-wet manner, the colored clear paint (6) containing particulate pigment in an amount of 0.5 to 5% by weight relative to the solid content of the colored clear paint, the particular pigment having a particle size in the range from 0.01 to 0.4 µm; and
- e) baking the colored clear paint (6) and colorless clear paint (7) to form a third coating layer on the second coating layer.
- 2. A method as claimed in claim 1, wherein step (a) comprises coating and baking the electrodeposition paint (2) before coating and baking the intermediate coat paint (3).
- 3. A method as claimed in claim 1 or 2, wherein step (b) comprises coating the base coat paint (4) before coating the colorless clear paint (5).
- 4. A method as claimed in any preceding claim, wherein step (d) comprises coating the colored clear paint (6) before coating the colorless clear paint (7).
- 5. A method as claimed in any preceding claim, wherein the base coat paint (4), the colored clear paint (6) and the colorless clear paints (5,7) are each formed of a synthetic resin selected from acrylic polyol and acrylic polyol modified with fluororesin, the resin preferably containing a hardener selected from melamine and isocyanate.
- 6. A method as claimed in any of claims 1 to 5, wherein the base coat paint (4) is in a red color system or a blue color system and contains aluminum powder in an amount of not more than 8% by weight relative to the solid content of the base coat paint.
- 7. A method as claimed in any of claims 1 to 5, wherein the base coat paint (4) is in a black color and contains aluminum powder in an amount of not more than 0.5% by weight relative to the solid content of the base coat paint.
- 8. A method as claimed in any preceding claim, wherein the colored clear paint (6) is in a red color system or a blue color system and contains particulate pigment having a particle size in the range from 0.2 to $0.4 \mu m$.
- 9. A method as claimed in any preceding claim, wherein the colored clear paint (6) contains particulate pigment in an amount in the range from 2 to 4% by weight relative to the solid content of the colored clear paint.
- 10. A method as claimed in any preceding claim, in which step (a) is applied to the surface of a steel plate (1) forming part of an automotive vehicle outer panel.

45

40

35

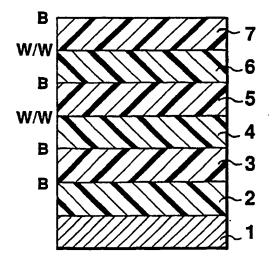
5

10

20

50

FIG.1





EUROPEAN SEARCH REPORT

	DOCUMENTS CONS	IDERED TO BE REL	EVANT		EP 90306405.	
Category		h indication, where accinopital ant passages		vant Iaim	CLASSIFICATION OF THE APPLICATION (Int. CIT)	
A	DE - A1 - 3 52 (KANSAI PAINT * Page 18, line 19 *	CO.) line 29 - page	20,		B 05 D 1/38 B 05 D 7/16 B 05 D 5/06	
A		estel Tele- ATIONS LTD.,				
A	EP - A2 - 0 23 (NIPPON PAINT * Pages 11-		1-5 *			
A	DE - A1 - 3 83 (KANSAI PAINT * Claims *		1		TECHNICAL FIELDS SEARCHED (Int CI')	
A	GB - A - 1 535 (DAI NIPPON TO * Totality	RYO CO.)	1		B 05 D	
Α .	US - A - 4 268 (SAKAKIBARA et * Totality	al.)	1			
	The present search report has b	een drawn up for all claims				
•	Place of search VIENNA	Date of completion of the 31-08-1990	ne search	SCHÜTZ		
Y : parti docu A : tech	CATEGORY OF CITED DOCL icularly relevant if taken alone icularly relevant if combined wument of the same category inclogical background -written disclosure	ith another D: 6	parlier patent doc ofter the filing dat document cited in document cited for	ument, bu e i the appli or other re	ng the invention It published on, or cation asons family, corresponding	